MICROCHEMISTRY OF SMALL DESERT VARNISH SAMPLES, WESTERN NEW SOUTH WALES, AUSTRALIA

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ABSTRACT

The chemistry of varnish scrapings from within and adjacent to rock engravings on sandstone outcrops in semiarid Australia was analysed using an electron microprobe (WDS mode). Small-area analyses were used to reduce potential contamination from identifiable within-varnish detrital grains and from substrate material. Ratios of (Ca + K):Ti were compared for rock engravings on older and younger rock surfaces, and between different engraving styles. Although ratios from varnish on the older surface were lower than for the younger surface, differences were not statistically significant. Sorting of analyses for potentially anomalous amounts of minor elements had little effect on the ranking of individual ratio values. Rankings of within-engraving ratio values were generally in accord with relative age expectations but differences between samples were not significant, with the chemical variability of varnish being high even without the contribution of discernible detrital inclusions. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Desert varnish is a naturally occurring coating on rocks in arid regions, usually having a thickness of less than 300 μm. The physical and chemical characteristics of varnish are extremely variable over distances of micrometres (Dorn and Oberlander, 1982; Dragovich, 1988), millimetres (Reneau *et al*., 1992) and kilometres (Reneau, 1993; Dorn *et al*., 1990). Varnish is composed mainly of silicate clays (Potter and Rossman, 1977) and iron and manganese oxides and hydroxides. Some of the minor and trace elements present within varnish – including potassium, calcium, titanium, phosphorus, sulphur, magnesium, sodium, copper and nickel (Lakin *et al*., 1963; Duerden *et al*., 1986) – have been examined for their potential to provide relative and absolute dating in both archaeological (Loendorf, 1991) and geomorphological (Dorn *et al*., 1986; Dorn, 1988; Peterson *et al*., 1995) contexts. By using a combination of chemical and morphological characteristics of the material, varnish has also been investigated as a palaeoclimatic indicator (Dorn, 1994).

The extent to which varnish chemistry is modified over time has been debated. Empirical associations have been found between varnish age and the ratio of the specified minor elements of calcium and potassium in relation to titanium (Dorn, 1983; Harrington and Whitney, 1987; Pineda *et al*., 1988; Whitney and Harrington, 1993), with lower ratios of (Ca + K):Ti being found in varnish on older surfaces. Dorn and Krinsley (1991) explained the apparent time-dependence of cation ratio changes as a function of leaching of the more mobile elements (calcium and potassium) from the varnish. The changes are apparently unidirectional, always leading to a lowering of the ratio due to a relative net loss of calcium and potassium. The alternative view is that varnish chemistry is determined by the nature of accreting material, rather than by post-depositional chemical modifications (Reneau *et al*., 1992). This interpretation provides for changes in varnish chemistry over time resulting from differing source materials, with recent varnishes not necessarily containing relatively more calcium and potassium than older varnishes. In this model, variations in varnish chemistry do not change regularly over time and thus cannot be used as a predictor of varnish age.

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Dorn and co-workers have analysed a large number of varnish samples, and the regularity and consistency of their cation ratio results have been explained by the time-dependence of microchemical modifications in carefully selected field samples. Misleading cation ratio results can arise from diverse sources, many of which have been identified (Krinsley *et al*., 1990). The absolute ages of varnishes have also been investigated by radiocarbon dating of organics trapped within or beneath the varnish (Dorn *et al*., 1986; Peterson *et al*., 1995) and these ages have been linked to cation ratios. The interpretation of varnish radiocarbon ages raises different questions which will not be discussed here.

Varnish characteristics may combine with sampling procedures to produce misleading cation ratio results. Removal of varnish in the field by scraping off thick varnish may lead to a dominance of near-surface varnish layers in which the abundance of titanium may be considerably higher, as noted by Bierman and Gillespie (1994) in areas of previous volcanic activity in western USA. Any inconsistencies in depth of sampling may thus result in cation ratios whose variation is not related to post-depositional chemical changes. Accidental inclusion of some substrate may also occur if the varnish is thin (Reneau and Raymond, 1991; Bierman and Gillespie, 1994). As scrapings are often amalgamated before chemical analysis (Dorn *et al*., 1990; Dorn and Meek, 1995; Bierman and Gillespie, 1994), any identification of substrate and detrital components can only be made during pre-analysis examination under a microscope.

The aim of this study was to investigate varnish chemistry, especially the ratio of (Ca + K):Ti, in known or inferred relative age situations. Efforts were made to minimize possible influences of non-varnish material at the macro- (substrate) and micro- (within-varnish detritus) scales by using small samples of varnish scrapings which were not amalgamated before analysis. Instead of examining the entire varnish deposit, small-area chemical analysis points were selected on the scrapings to include the varnish ‘matrix’ or ‘cement’ and to exclude as much other material as possible, an approach which has not been previously attempted. The results were then examined to establish whether element ratios of varnish were in accord with archaeological (rock engraving) and geomorphic evidence regarding the relative chronology of rock surface exposure.

METHODS

Sample collection

Samples were collected in an area of sandstone outcrops located about 130 km northeast of Broken Hill in semiarid western New South Wales. Annual rainfall at Broken Hill (31°58′S latitude and 141°27′E longitude) is very variable: the long-term average annual rainfall is 224 mm, with yearly amounts ranging from 57 mm to 839 mm. Temperatures are high in summer and cool in winter, with daily mean minima and maxima ranging from 19·8°C to 33·3°C respectively in January and from 4·8°C to 14·5°C in July.

The main engraved rock outcrop at the study site is composed of coarse- to medium-grained quartz sandstone, with beds dipping at 20 to 25°. In addition to quartz, the rock also contains minor amounts of limonite, gypsum and muscovite, the latter being partly altered to kaolinite. The engravings included in this study occurred on case-hardened (‘silicified’) rock surfaces, located within a Heritage Site from which field samples of normal size cannot be collected. As engravings had been made on extensive rock outcrops, rather than on boulders or small stones, post-varnish burial was unlikely and overturning of the sampled varnish was not possible. Large numbers of rock engravings are present at the site: on one block of rock alone, McCarthy and Macintosh (1962) identified 304 individual items. Although relative engraving chronologies have been proposed on stylistic grounds (Maynard, 1979), varnish characteristics may provide additional information on which to base a relative age sequence.

Only small varnish samples could be used in this study, for the following reasons.

(1) Samples were collected from within and adjacent to Aboriginal rock engravings. As rock engravings are protected from any unauthorized interference by Heritage Legislation, only scraping which resulted in very inconspicuous changes to engravings was possible. Samples were taken with permission of the relevant Government authority and the local Aboriginal community.

(2) Varnish cover was very patchy and thin. In order to compensate for the relatively low potential amounts of varnish available for sampling, and to reduce the possibility of collecting varnish fragments with unique chemistry, scrapings were taken from at least three separate small areas for each sample.

(3) Sampling was directed towards obtaining information about engravings, so the varnish available within and adjacent to these microsites was the material that had to be sampled. Unfortunately, engravings were not located on the relatively few positions within the area where shiny, and possibly thicker, varnish had developed.

Samples were collected to evaluate chemical differences in varnish found in several situations: within and adjacent to Aboriginal rock engravings, within engravings found on rock surfaces of different ages, and within stylistically different engravings. For all small samples, scraping attempted to avoid spots of optically visible organisms such as larger microcolonial fungi (Dragovich, 1993) on the varnish surface. Lichens were absent from all microsites but microcolonial and other fungi and bacteria were probably not.
The following microsites were sampled.

(a) Two Aboriginal rock engravings, having a pattern of circles and described as ‘Panaramitee’ style by archaeologists (Maynard, 1979). This style occurs throughout arid and semiarid Australia, and was probably used over a prolonged time period, possibly from 1500 years to at least 40 000 years BP (Nobbs and Dorn, 1993). Very small varnish samples were collected from within and adjacent to each of the two engravings (a total of four samples): Engraving 1, samples A and B; and Engraving 2, samples C and D.
(b) Another two Panaramitee-style engravings on rock surfaces of geomorphologically different ages. An upper, older rock surface had been engraved with a series of ‘eggs?’ (sample G); and a lower surface, from which the upper (older) rock layer had been detached, was engraved with ‘tracks’ (sample H). Very small varnish samples were collected from within each of these engravings. It was assumed that engravings were made successively as rock surfaces became exposed rather than all at one time after all surfaces were exposed.
(c) Engravings of human figures, which archaeologists describe as belonging to a ‘Simple Figurative’ style that post-dates the early Panaramitee (Maynard, 1979). Sample F was collected from within these engravings.
(d) At a distance of about 1 km from the general area of collections outlined above, a further small sample adjacent to a rock engraving (sample E).
(e) A non-scraped field sample of varnished rock was collected from a rock outcrop about 5 km from the engraving site (sample I). This sample was large enough for the rock to be sectioned normal to the varnished surface, allowing for the varnish/substrate boundary to be clearly identified.

Sample analysis

The fine scrapings constituted very small total samples which were first examined under a microscope (×30 to ×60 magnification) to remove any obvious substrate material. The scrapings were not amalgamated by fusing into a single mass, as any substrate contamination remaining in the sample would then become undetectable. Instead, the scrapings were embedded in resin and polished. No quantitative screening of varnish scrapings for non-varnish material was attempted. However, before electron microprobe analyses were undertaken, two qualitative procedures were followed.

(1) Examination of BSE images of varnish scrapings. Different reflectance and particle morphology allowed for an initial general discrimination between varnish ‘matrix’ and within-varnish detritus or substrate material.
(2) EDS traces were taken on positions of probable or possible varnish ‘matrix’, in order to check for potential substrate contamination or the presence of within-varnish detrital material. Before probe analyses were undertaken, the EDS traces were used to verify that first, the normal combination of varnish elements was present (Si, Al, Fe, Mn, Ca, K, Ti); and second, the usual varnish elements were present in approximately their normal proportional ranges. High proportions of Si, Fe, P, Al, S, Ca or K – or very low amounts of Si, Al or Fe – indicated the probable presence of material other than varnish ‘matrix’. The only exception made to these general sorting procedures was the inclusion of analysis points where MnO was absent or present in small amounts. Earlier analysis of the field sample (Sample I) had shown within-varnish bands having alternately high and very low contents of MnO.

Table I. Mean oxide weight percentage of analyses of eight 'scraping' samples (A to H) and one field sample (I). Only analyses containing MnO are included. Analyses were obtained using an electron microprobe with a wavelength dispersive spectrometer

	A (10)	B (13)	C (10)	D (16)	E (17)	F (14)	G (5)	H (8)	I (13)
Na_2O	0·29	0·39	0·38	0·66	0·39	0·63	0·32	0·19	0·33
MgO	1·83	1·53	1·69	1·39	1·91	1·92	1·88	1·33	1·43
Al_2O_3	25·69	22·62	25·05	21·18	25·82	23·18	27·11	22·39	25·99
SiO_2	48·71	50·94	41·98	51·65	48·62	50·15	53·54	56·38	45·19
P_2O_5	1·56	1·67	1·21	1·58	1·34	0·78	0·43	1·01	n.a.
SO_3	0·77	0·73	0·49	0·86	0·73	0·95	0·25	0·34	n.a.
K_2O	2·75	2·38	2·48	2·37	2·85	1·54	2·08	1·69	2·37
CaO	2·13	1·78	0·73	0·81	1·46	0·55	0·52	0·42	0·31
TiO_2	1·15	1·07	0·97	0·90	1·17	0·81	1·43	1·14	0·87
BaO	0·15	0·28	0·91	0·38	0·11	0·41	0·11	0·23	0·21
MnO	1·42	1·94	11·77	4·91	1·58	6·72	1·53	4·31	8·44
Fe_2O_3	13·55	12·48	12·35	13·30	14·03	12·36	10·80	10·57	14·86
Total	100	100	100	100	100	100	100	100	100

Legend: A=within Engraving 1; B=adjacent to Engraving 1; C=within Engraving 2 – includes one analysis with 38·1 per cent MnO; D=adjacent to Engraving 2; E=adjacent to engraving, 1 km distant; F=within engraving of human figures; G=within engraving on Older surface; H=within engraving on Younger surface; I=normal field sample, 5 km distant; (*x*)=number of analyses containing MnO; n.a.=not analysed

Independent standards were used on the electron microprobe to calibrate analyses before and during analytical sessions. Already-analysed points were periodically re-analysed as an additional check on calibrations. Wavelength dispersive spectrometry was used to analyse eight small samples at a total of 120 separate points, using a spot size of 2 to 5 μm. The normal field sample of varnished rock was sectioned and embedded; this varnish showed laminations in cross-section. Due to the small size and lack of orientation of the scrapings, it was not possible to identify whether laminations were present in the scrapings as well. Thirteen analyses were undertaken on varnish in the sectioned field sample. Results from all analyses were normalized to 100 per cent to allow for between-sample comparisons, and the ratio (Ca + K):Ti was determined for each analysis.

RESULTS AND DISCUSSION

Average oxide weight percentages for a total of 133 electron microprobe analyses on eight small samples (scrapings) and one normally sized field sample are presented in Table I. In comparison with varnish chemistry reported in other studies (e.g. Dorn *et al*., 1990; Dragovich, 1988; Nobbs and Dorn, 1993; Reneau *et al*., 1992), mean manganese levels were often relatively low, with 41 analyses registering less than 1 per cent MnO. No manganese was recorded in a further 28 analyses. The normal field sample (sample I) had MnO values for individual analyses ranging from 18 per cent to less than 1 per cent. For all analyses containing manganese, mean MnO levels ranged from 0·5 up to 12 per cent. The variable and relatively low MnO levels in many samples lay within the range of values recorded for some individual layers in the field sample (sample I). Low MnO layers may have been disproportionately represented in the scrapings but this could not be substantiated. Although gypsum was present in the substrate, SO_3 contents for all samples averaged less than 1 per cent and mean CaO levels were not notably high.

Mean element ratios of (Ca + K):Ti for individual samples ranged from 3·06 to 5·64, with large standard deviation values being recorded for all but one sample (sample G). The large variance was an expected difficulty with these analyses, due to the inherent chemical variability of varnish (Dragovich, 1988; Reneau *et al*., 1992). The procedures taken to minimize the possible inclusion of detrital or substrate material in analyses apparently did not reduce this variability. Of more specific relevance to analysis of very small samples, Bierman *et al*. (1991) found that scanning electron microscope (SEM) analysis of *in situ* varnish yielded an increase in the variance of cation ratios with decreasing areas of analysis. The combination of variable varnish chemistry and small sample size proved problematic. If element ratios were to be linked with relative varnish ages, differences in between-sample element ratios needed to be large and have a pattern that was consistent with known or inferred varnish chronologies. Element ratio results for each sample in this study are presented as

Table II. Ratios of (Ca + K) : Ti for nine samples. Mean ratios are listed for all analyses, and then separately for analyses with and without MnO, without potentially anomalous compositions, and without anomalies but including only those with Mn : Fe > 0·3

	A	B	C	D	E	F	G	H	I
All									
mean	5·56	5·64	5·03	4·94	5·02	4·37	3·06	3·82	4·25
	(10)	(13)	(14)	(16)	(20)	(17)	(12)	(18)	(13)
All without Mn									
mean			5·73		5·44	5·72	3·27	4·37	
	0	0	(4)	0	(3)	(3)	(7)	(10)	
All with Mn									
mean	5·56	5·64	4·75	4·94	4·95	3·99	2·76	3·13	4·25
s.d.	2·25	1·83	1·18	1·19	1·27	1·61	0·82	1·66	0·97
	(10)	(13)	(10)	(16)	(17)	(14)	(5)	(8)	(13)
With Mn (less exclusions; see text)									
mean	4·30	4·92	4·75	5·03	4·65	3·99	3·12	3·39	4·25
s.d.	1·04	1·74	1·18	1·17	1·14	1·61	0·45	1·61	0·97
	(7)	(9)	(10)	(15)	(14)	(14)	(4)	(7)	(13)
With Mn (less exclusions and with Mn : Fe > 0·3)									
mean	4·26	5·15	4·56	5·03	3·99	3·95	3·09	3·26	4·42
	(2)	(6)	(9)	(15)	(6)	(11)	(2)	(4)	(10)

Legend: A=within Engraving 1; B=adjacent to Engraving 1; C=within Engraving 2 – includes one analysis with 38·1 per cent MnO; D=adjacent to Engraving 2; E=adjacent to engraving, 1 km distant; F=within engraving of human figures; G=within engraving on Older surface; H=within engraving on Younger surface; I=normal field sample, 5 km distant; (*x*)=number of analyses containing MnO; s.d.=standard deviation

a mean for all points analysed, as well as separate listings for those with, and without, manganese (Table II). For samples where manganese was not present in all analyses, the mean element ratio was always higher for the group without manganese than for those containing manganese.

Further sorting of probe analyses was undertaken by excluding possibly anomalous analyses. No analysis was eliminated on the grounds of being chemically different from the normal field sample, as this would have presupposed that the field sample was representative of all varnish collected. The following four criteria were used to exclude possibly anomalous analyses.

(1) Where the percentage CaO exceeded that of K_2O. Mean oxide weight percentage of K_2O was between 1·3 and 4·3 times that of CaO for the eight small samples, so a reversal of relative abundance would indicate an unusual chemical composition. A total of nine analysis points in three separate small samples were excluded under this criterion.
(2) Where P_2O_5 exceeded 3 per cent. This was an arbitrary value which excluded a further four analysis points. A high phosphorus content could indicate contamination from substrate or within-varnish detrital material, or the presence of fungi.
(3) Where SO_3 exceeded 3 per cent. Large amounts of SO_3 could indicate substrate contamination from gypsum (unlikely in the single analysis excluded, as it had low amounts of calcium), detrital material, or the presence of fungi. The threshold value was arbitrarily chosen and excluded one additional analysis.
(4) Where TiO_2 exceeded 2·5 per cent. This excluded two analyses, one from each of the engravings on geomorphic surfaces of different ages. High levels of titanium are most likely to be derived from detrital or substrate material.

When the above exclusions were made, absolute values of mean element ratios changed but the pattern of higher and lower ratios for each comparative test remained the same. For example, higher ratio values were recorded within the engraving on the younger rock surface than the older surface for the categories of ‘All’, ‘All with Mn’ and ‘Mn group less exclusions’.

In the final sorting, analysis points were removed if the Mn:Fe ratio was not >0·3 (Table II). Detailed age testing has only been conducted on varnishes with a ratio of Mn:Fe > 0·3 (Krinsley *et al*., 1990), partly because

cation ratios did not change with time in a regular pattern in varnishes having Mn:Fe ratios of <0·1 (Krinsley *et al*., 1990). This manipulation involving Mn:Fe ratios, although leaving few points in some categories, resulted in changed absolute mean values but a similar pattern between compared samples, as outlined below.

(1) *Relative ratios of varnish within and adjacent to engravings*. If the rock were varnished at the time of engraving manufacture, varnish on adjacent rock surfaces would be older (= lower ratio) than within-engraving varnish. Results from both Engraving 1 (samples A and B) and Engraving 2 (samples C and D) were the reverse of this, with higher mean ratios on adjacent rock (for 'All with Mn', 'Mn group less exclusions' and 'Mn group less exclusions and Mn:Fe>0·3'). However, the relatively small differences between the means and the variability within samples resulted in no statistically significant difference (Mann Whitney U test) between the 'within' and 'adjacent' pairings. The additional 'adjacent' sample from a surface about 1 km away had an element ratio similar to the others. Even though 'within/adjacent' comparisons did not produce the expected relativities, no substantial numerical differences in mean element ratios were recorded.

(2) *Relative ratios within engravings on Younger and Older surfaces*. Element ratios were consistently lower within the engraving on the Older (sample G) than on the Younger surface (sample H). This was the case for all sortings ('All', 'All with Mn', 'Mn group less exclusions' and 'Mn group less exclusions and Mn:Fe>0·3'), as well as for the 'Without Mn' group. Variability within the analyses for the Younger surface was large, contributing to the absence of a statistically significant difference between the samples (Mann Whitney U test).

(3) *Relative ratios within figures and other engravings*. The determination of element ratio values from different within-engraving varnishes allowed for comparisons between varnishes which formed and are persisting under microenvironments that are similar in terms of moisture retention, potential for trapping of detrital material, and possibilities for presence of micro-organisms. The exceptions were the human figures (sample F) which, unlike the other engravings, were located on a near-vertical rock face.

The ranking of element ratios within engravings had a consistent pattern for all the sortings, with the exception of Engraving 1 (sample A) for the 'All with Mn' group which included three analyses having $CaO>K_2O$. Engraving 1 (sample A) and Engraving 2 (sample C) always had higher ratios than the human figures (sample F), followed by engravings on the Younger surface (sample H) and then the Older surface (sample G) (Table III). Apart from the human figures, all engravings were Panaramitee style. Panaramitee samples thus included those with both the highest and the lowest values, suggesting a prolonged period of engraving manufacture, which agrees with archaeological interpretations (Maynard, 1979; Nobbs and Dorn, 1993). Within-engraving ratios ranged from 2·76 to 5·56 for all analyses with MnO, and from 3·09 to 4·56 with all exclusions. No statistically significant differences (Mann Whitney U test) were found between element ratios for the human figures and either of the two sets of Panaramitee engravings (circles, and those on the Younger and Older surfaces). The only significant difference recorded between element ratios was for the extreme values – one of the Panaramitee circles (sample A) and the engraving on the Older surface (sample G). Unlike the situation reported by Pineda *et al*. (1988) in southern Africa, no pattern of increasing standard deviations with decreasing ratios was found.

Relative age controls were clearer for the geomorphic than for the archaeological situations. The Older and Younger surfaces are adjacent to one another on the same large, gently sloping outcrop; the Panaramitee circle engravings lie within 30 m on the same outcrop. In contrast, the human figures appear on a vertical face of a separate outcrop. An additional difficulty with the relative ages of the human figures and the Panaramitee circles is that the Panaramitee style extended over a prolonged period. It is probable that human motifs were being engraved contemporaneously with the more recent of the Panaramitee engravings; that is, animal tracks and circles (Panaramitee style) may be relatively old or relatively young, while human figures are all likely to be relatively young. Figure 1 provides a summary of mean element ratios for geomorphic and archaeological surfaces.

The relative age sequence of engravings on the Older surface, the Younger surface, and the human figures seems reasonable, as does the sequence of Older surface, Younger surface, and circles. The relative element ratio positions of the human figures and the circles is less satisfactory. Even though archaeological arguments

Table III. Engravings ranked according to within-engraving varnish ratios of (Ca+K):Ti. Rankings are from the highest ('youngest') to the lowest ('oldest') value

	All analyses	With Mn	Mn less excl.	Mn less excl. and Mn:Fe>0·3	Without Mn
	Engraving 1 (A)	Engraving 1 (A)	Engraving 2 (C)	Engraving 2 (C)	n.a.
	Engraving 2 (C)	Engraving 2 (C)	Engraving 1 (A)	Engraving 1 (A)	Engraving 2 (C)
	humans (F)	humans (F)	humans (F)	humans (F)	humans (F)
	Younger (H)	Younger (H)	Younger (H)	Younger (H)	Younger (H)
	Older (G)	Older (G)	Older (G)	Older (G)	Older (G)
Ratios					
highest	5·56	5·56	4·75	4·56	5·73
lowest	3·06	2·76	3·12	3·09	3·27

n.a.=Not applicable. All analyses for sample A contained MnO. (A)=sample identification

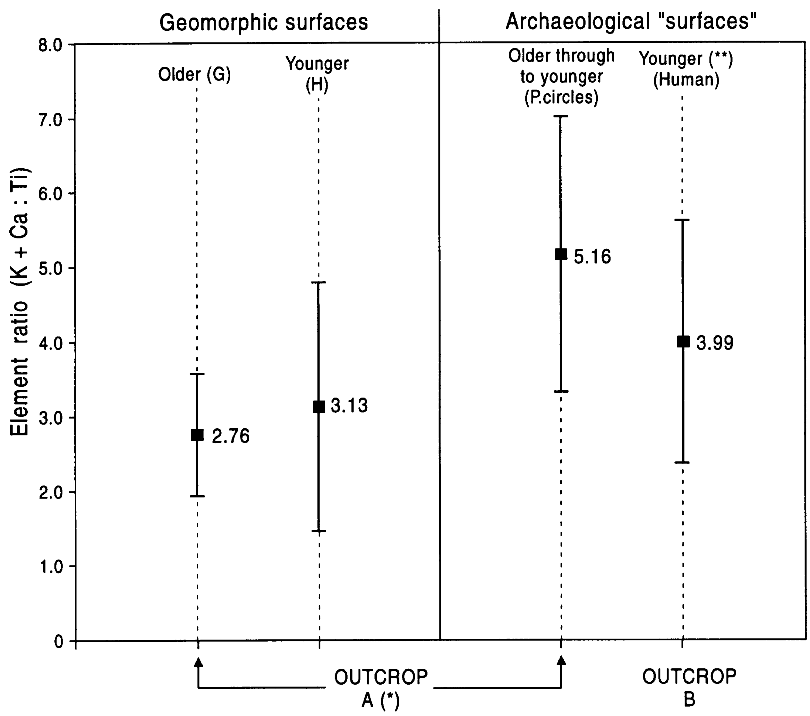

Figure 1. Element ratios of all within-engraving varnish samples which contained MnO. The bars represent one standard deviation from the mean. (*) Three sampled engravings were located on an extensive gently sloping surface of Outcrop A. Outcrop B is a small separate outcrop, with engravings on a vertical rock face.
(**) Archaeologists consider that early Panaramitee engravings are older than the human figures. More recent Panaramitee would have temporal overlap with figurative engravings

could place the human figures as either older, younger, or contemporaneous with the circles, macroscopic weathering and sharpness of engraving edges suggest that the human figures were more recently engraved. Apart from this, rankings of within-engraving element ratios generally do not appear to contain gross anomalies. The minor between-sample differences and large within-sample variation in ratios provide the major obstacle to definitive conclusions about their usefulness as indicators of relative chronologies.

Discussion

The procedures adopted to minimize the inclusion of detrital and substrate material involved the need to seek out and check appropriate analysis points, rather than setting the probe on a predetermined grid for automatic analysis. This made analysis a time-consuming process and acted as a constraint on the total number of analyses

in the data set. As a result, when analyses were sorted according to different criteria, some individual categories often contained few analyses. If the results reported here followed the pattern found by Bierman *et al*. (1991), additional analyses would have reduced ratio variability but made only a small change to mean ratio values. Larger numbers of analyses would have been desirable given the variability in chemical composition of the varnish. Although variability was expected, its magnitude as found in matrix analyses demonstrated that chemical variability of varnish is not solely a function of detrital inclusions.

An important aim of this study was to analyse only the ‘matrix’ or cementing material of varnish, which contains silicate clays and oxides that may behave as a cation exchange complex (Dorn and Whitley, 1983). The cation ratio dating methodology, however, excludes only detrital material which is large enough to be identified under ×40 magnification, and small detrital grains may be included in ‘bulk’ varnish samples. Titanium, for example, is not uniformly distributed but has been found in X-ray maps (Bierman and Gillespie, 1994) to occur in discrete locations within some varnishes. The question of what constitutes material capable of acting as a cation exchange complex, and what material is excluded, is important both in terms of the appropriate descriptor (as a ‘cation’ ratio or an ‘element’ ratio) and in relation to the processes leading to chemical changes over time. If fine within-varnish detrital grains are included in the measurement of a cation ratio, chemical alteration of these grains over time may be contributing to changing ‘bulk’ ratio values; that is, decreasing cation ratio values may be partly reflecting weathering of minerals within the varnish, rather than only the loss of cations from (clay) exchange complexes. Information on the weathering patterns of detrital grains may be obtained from detailed examination in a high resolution transmission electron microscope (HRTEM), as used by Krinsley *et al*. (1995) to identify the microdivision of clay minerals within varnish.

The interpretation of probe analyses and, more particularly, whether individual analyses were judged to be ‘uncontaminated’ varnish material or not, proved problematic despite pre-analysis microscope checking and assessment of BSE images and EDS traces. Although predominantly non-varnish materials can be identified, analyses of varnish which contain some additions, either from occasional within-varnish detrital grains or the underlying rock, are more difficult to recognize unequivocally. The amount of detrital inclusions in samples included in this study may thus have been greater than identified. In southwestern USA, Reneau *et al*. (1992) described varnish which was relatively poor in manganese and with little detritus as having a strong relationship between amounts of Mn and Ca ($r = 0{\cdot}72$). Detritus-rich varnish, in contrast, had weak associations between these two elements, a result similar to that found in the small samples used in this study. The sandstone provided a microtopographically irregular surface which was likely to trap detritus in microdepressions, probably leading to a high ratio of detritus to matrix within the varnish. However, it is unclear why such detrital material was not recognized in the pre-analysis examination of points chosen for analysis. Explanations may include the detrital material in the scrapings being silt- or clay-sized, preventing its identification; or the links between Mn and Ca relationships and detrital abundance may not hold for varnish in all environments.

SUMMARY AND CONCLUSIONS

Small-area analyses, undertaken to minimize potential contamination from the varnish substrate and within-varnish detrital material, were used to determine ratios of (Ca + K):Ti in varnish within and adjacent to rock engravings. The morphology of varnish scrapings was examined in a backscattered electron image and chemical composition checked in EDS scans before chemical analysis in an electron microprobe. Chemical analysis data were treated in two ways: first, by assuming that all analyses undertaken were varnish cement; and second, by sorting these results to exclude analyses possibly containing detrital or substrate material. The sorting procedures produced few changes to the relative values of paired comparisons (‘within/adjacent’ or ‘older/younger surface’). Although actual ratio values altered, the ranking of values for samples from the Younger and Older surfaces and the human figures remained the same throughout, regardless of exclusions.

The ranking of mean element ratios for within-engraving positions was consistent with archaeological and geomorphic interpretations. However, differences in mean element ratios between sampled pairs were not significant, with results showing small between-sample differences and large within-sample variability in ratios. These ratio results on apparently ‘matrix’ material indicate that chemical variability in varnish is not

solely a function of detrital inclusions. Large differences in mean element ratios between varnish on surfaces of different geomorphic ages were not found.

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